

## MUTUAL SOLVENT FOR IMPROVED OIL AND GAS PERMEABILITY

### BACKGROUND OF THE INVENTION

01 Paraffinic and asphaltenic hydrocarbons, as well as calcium carbonate and clays, may form undesirable deposits in boreholes and equipment used for the production of oil and gas from underground formations. The problem of removing such deposits is discussed in US patent nos. 5,152,907 and 6,242,388, and typically involves using an aqueous solution of an acid, such as hydrochloric acid, hydrofluoric acid, acetic acid, and the like, and mixtures thereof, in combination with a mutual solvent of oil and water. A challenge in the art of acidizing wells is to provide a solvent system with a mutual solvent that is effective in cleaning wells and production equipment, while being economical and environmentally friendly.

### SUMMARY OF THE INVENTION

02 There is therefore provided a solvent system for use in acidizing and cleanup in oil wells and gas wells. The solvent system comprises a combination thereof, a substantially water-soluble alcohol, such as methanol, or ethanol or any mixture thereof, a substantially water / oil-soluble ester, such as one or more  $C_2 - C_{10}$  esters and a substantially water / oil-soluble ketone, such as one or more  $C_2 - C_{10}$  ketones. A preferred ketone solvent is methyl ethyl ketone. A preferred substantially water-soluble alcohol is methanol. A preferred substantially water / oil-soluble ester is methyl acetate.

03 The ketone solvent may be present in an amount from 10 wt % to about 50 wt %; the substantially water soluble alcohol, in an amount within the range of about 5 wt % to about 50 wt %; and the substantially water/ oil-soluble ester in an amount within the range of about 5 wt % to about 50 wt %, each amount being based upon the weight of the solvent system.

04 The preferred ketone solvent may be present in an amount from 40 wt % to about 50 wt %; the substantially water-soluble alcohol, in an amount within the range of about 20 wt % to about 30 wt %; and the substantially water / oil-soluble ester, in an amount within the range

of about 20 wt % to about 30 wt %, each amount being based upon the weight of the solvent system.

05 Further summary of the invention is found in the claims, which are incorporated by reference here.

#### DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS OF THE INVENTION

06 The term "comprising" is used in its inclusive sense, and does not exclude other components being present. The terms "water soluble" and "oil soluble" mean substantially water and oil soluble respectively. All percentages used herein are weight percent of the total weight of the ester, alcohol and ketone/cyclic ether components of the solvent system, in the cases where no acid is present, and weight percent of the total weight of the acid, ester, alcohol and ketone/cyclic ether components of the solvent system, in the cases where acid is present.

07 The preferred components for this solvent system for use in oil and gas well operations are a water/oil soluble ester, a water-soluble alcohol, and a water/oil-soluble solvent, either or both of a ketone or cyclic ether. The water/oil soluble ester may be methyl acetate, present in the amount of about 5 wt% to 50 wt%, for example 25 wt %, and the water-soluble alcohol may be methanol, present in the amount of about 5 wt% to 50 wt%, for example about 25 wt %. If a water/oil soluble ketone is used, it may be methyl ethyl ketone (acetone) present in the amount of about 10 to 50 wt %. The water/oil soluble ester may be methyl acetate present in the amount of about 25 wt %.

08 Instead of methyl ethyl ketone, a water/oil soluble cyclic ether may be used, for example from about 5 wt% to about 50 wt % tetrahydrofuran. A combined amount of the cyclic ether and ketone may be present in the amount of from about 5 wt% to about 50 wt%.

09 The water/oil-soluble ketone may be a mixture of  $C_3 - C_{10}$  ketones. The water/oil-soluble ester may be a mixture of  $C_2 - C_{10}$  esters. The water/oil soluble cyclic ether may be a mixture of  $C_2 - C_{10}$  ethers.

10 An aqueous acid may be added to the solvent system. For example the acid may be present in the amount of 5 wt% to 50 wt%. With 50 wt% hydrochloric acid 15%, the water/oil soluble ester may be about ethyl acetate present in the amount of 12.5 wt%, the water-soluble alcohol may be methanol present in the amount of about 12.5 wt %, and the water/oil soluble-ketone may be about methyl ethyl ketone present in the amount of about 25 wt%.

11 In another example, the solvent system may comprise about 12.5 wt % methyl acetate, about 12.5 wt % methanol, about 25 wt % methyl ethyl ketone and about 50% wt% hydrochloric acid 15%. The ketone may be replaced by an equal weight of tetrahydrofuran. Other water soluble inorganic and organic acids may be used for the aqueous acid.

12 Example: A scale example was prepared by adding 10g of heavy oil (density = 985 kg/m<sup>3</sup>) to calcium carbonate (15g). The scale sample was mixed thoroughly and allowed to age overnight. The scale sample was then weighed out in 2 to 4 g sizes and added to a 100 ml solution (listed below) and the reactions were observed.

Alcohol	Ester	Ketone / Ether	Acid	Observations
			15% HCl (100%)	No oil separation, no effervescence
Methanol (25%)		THF (25%)	15% HCl (50%)	Complete oil separation/effervescence in 20 mins
Methanol (25%)		THF (12.5%)/Acetone (12.5%)	15% HCl (50%)	Incomplete oil separation after 30 mins

Methanol (12.5%)		THF (18.75%)/Acetone (18.75%)	15% (50%)	HCl	Complete oil separation/effervescence in 25 mins
		THF (10%)/Acetone (40%)	15% (50%)	HCl	Complete oil separation/effervescence in 10 mins
		THF (7.5%)/Acetone (42.5%)	15% (50%)	HCl	Complete oil separation/effervescence in 15 mins
		THF (5%)/Acetone (45%)	15% (50%)	HCl	Complete oil separation/effervescence in 20 mins
Methanol (16.5%)	Methyl acetate (33.5%)		15% (50%)	HCl	Complete oil separation/effervescence in 15 mins
Methanol (8.25%)	Methyl acetate (16.75%)	THF (12.5%)/Acetone (12.5%)	15% (50%)	HCl	Complete oil separation/effervescence in 11 mins
Methanol (13.6%)	Methyl acetate (26.4%)	MEK (10%)	15% (50%)	HCl	Complete oil separation/effervescence in 7 mins
Methanol (8.25%)	Methyl acetate (16.75%)	MEK (25%)	15% (50%)	HCl	Complete oil separation/effervescence in 5 mins
Methanol (10.4%)	Methyl acetate (38.8%)	THF (0.8%)	15% (50%)	HCl	Incomplete oil separation after 30 mins

Methanol (7.8%)	Methyl acetate (29.1%)	THF (0.6%) / MEK (12.5%)	15% HCl (50%)	Complete oil separation/effervescence in 15 mins
Methanol (5.2%)	Methyl acetate (19.4%)	THF (0.2%) / MEK (25%)	15% HCl (50%)	Complete oil separation/effervescence in 5 mins
Methanol (17%)	Methyl acetate (20%)	THF (0.5%) / MEK (12.5%)	15% HCl (50%)	Complete oil separation/effervescence in 15 mins
Methanol (10.5%)	Methyl acetate (14%)	THF (0.5%) / MEK (25%)	15% HCl (50%)	Complete oil separation/effervescence in 4 mins

13 Immaterial modifications may be made to the invention described here, without departing from the invention as defined by the claims.